<u>**STATISTICAL THERMODYNAMICS**</u>
<u>**INTRODUCTION**</u>
Objectives

1. Be able to explain what statistical mechanics is and why it is important.
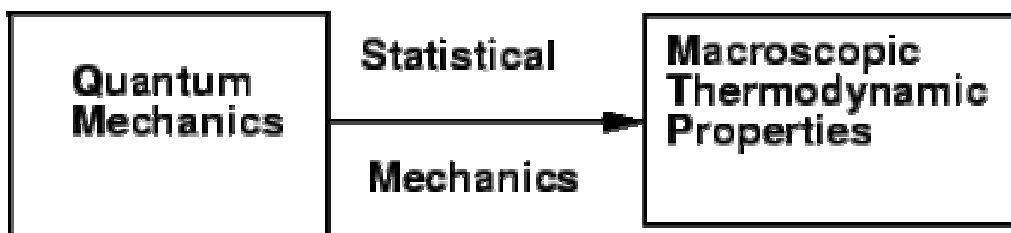
2. Basic tools of Statistical Mechanics

<u>Introduction to Statistical Mechanics</u>

Q1: What is Statistical Mechanics?
Thermodynamics deals with the macroscopic properties of matter. Thermodynamics is not dependent on the fundamental nature of matter. That is, thermodynamics is valid whether matter is made up of atoms and molecules or whether matter is made up of some kind of continuum fabric.
Quantum mechanics deals with the behavior of matter on the microscopic scale. In quantum mechanics we calculate the energy and behavior of a few atoms or small molecules. Most calculations are performed at $T = 0$ K. We can't get the macroscopic properties (e.g., the equation of state, etc.) from Quantum mechanics.
Statistical mechanics is a bridge between quantum mechanics and thermodynamics. We seek to use statistical mechanics to compute macroscopic properties from the quantum mechanical information about the atoms and molecules of interest.

Q2: Why study statistical mechanics?
Consider an example: We have used equations of state (EOS). What are they? They give you a method of calculating one of (*P, V, T*) given any two of them. Usually EOS are cast in some analytic functional form. How do you get EOS?

I.   Guess some functional form, $P = f(V, T)$. e.g., van der Waals made the guess that $P=RT/(V-b) – a/V^2$.

II.   Measure as much *PVT* data as you possibly can *for a specific fluid.*

III.   Regress the parameters in the EOS in some least squares fashion. e.g., find a and b the van der Waals EOS for the fluid.

Do you now have complete information? How about *U, H, S*, etc.?
What happens if you want to find the EOS of a different fluid? For example, you did the above for propane, now you want the EOS for H_2O. In many cases you need to go back to the beginning, i.e., guess a *new* functional form. This is because you can't fit propane and water with the same functional form.
Problems with the above process:

i.   Very time consuming and very expensive.

ii.   Have to start all over again for many new fluids.

iii.   Extrapolation outside the region of parameter regression is not valid. Extrapolation often gives unphysical results. For example: What happens in the van der Waals EOS if $V = b$?

iv.   This process does not give you any physical insight about why the fluid behaves as it does, or how to systematically improve the EOS.

v.   You don't know anything about many of the other properties.

Is there some way we can get at the EOS from a fundamental approach? If matter is truly composed of molecules, then it must be the interactions among these molecules that give rise to the macroscopic observable behavior.

POSTULATE: If we can understand the microscopic interactions we can predict the macroscopic behavior. This is the goal of statistical mechanics. Statistical mechanics relies on determining the most probable distribution of quantum microstates in macroscopic system.

Notes:

1- For a macroscopic system, define *N, V*, and *U* as the Number of particles, volume and the total energy of the system respectively. The *thermodynamics limit* defined as $V \rightarrow \infty$ and $N \rightarrow \infty$, then the particle density $v = N/V$ is a fixed quantity at a preassigned value.

2- The microscopic states are defined by two group of parameters

a- $\varepsilon_1, \varepsilon_2, ...$ These discrete energies possessed by a single particle, which obtain by solving the wave equation.

b- $N_1, N_2, ...$ being the number of particles in this energy state respectively. Hence (for non-interacting particles) $N = \sum_i N_i$, and $U = \sum_i N_i \varepsilon_i$ where N_i is the number of particles with energy ε_i.

$$\varepsilon_i \equiv \begin{array}{ll} Classically & \Rightarrow U \text{ is contiuous} \\ Quantum\ M. & \Rightarrow U \text{ is discrete} \end{array} \quad , \quad (1)$$

$\Delta \varepsilon = \varepsilon_i - \varepsilon_j << U$, We might regard U as almost a continuous variable. The specification of the actual values of the macroscopic parameters *N, V*, and *U* (i.e. *T*) then defines a particular *microstate* of the given system. Notice that, at the molecular level there will be a large of different ways in which the total energy of the system can be distributed among the *N* particles constituting it. Each of these (different) ways specifies a particular *microstate*, or *complexion*, of the given system.

The whole theory of statistical mechanics is based upon the following postulates:

A- For each complexion there is a probability "*w*" that measure the number of ways in which we can produce it under the conditions (a) and (b).

B- The most probable distribution is that of maximum probability:

$$\frac{\partial \ln w}{\partial N_i} = 0$$

C- Entropy (S) measure the disorder of the system through the relation:

$$S = k \ln w,$$

where k is the Boltzmann's constant and w is the actual number of microstates for a given system. The entropy has the following properties:

i-   The entropy for a simple system is a continuous, single-valued, differentiable, homogeneous-first-order function of the extensive parameters (N,V,U), and monotone increasing in U.

ii- The entropy of a composite system is the sum of the entropies of the constituent subsystems: $S(N,V,U) = \sum_i S_i(N_i,V_i,U_i)$.

iii- The entropy should be maximum at equilibrium.

iv- The entropy of a simple system approaches zero as $T \to 0$, or $\left(\frac{\partial U}{\partial S}\right) \to 0.$

Examples: The following expressions are acceptable expressions. (R, N_o, V_o, U_o) are constants.

$$a. \quad S = R\left(\frac{UVN}{U_o V_o N_o}\right)^{1/3}$$

$$b. \quad S = R\left[\left(\frac{UN}{U_o N_o}\right)^2 \frac{V}{V_o}\right]^{1/5}$$

$$c. \quad S = R\left(\frac{UN}{U_o N_o}\right)^{1/2} Exp\left[-\left(\frac{VN_o}{V_o N}\right)^2\right]$$

D- Equal a Priori Probability: *a priori* from the Latin, meaning ``conceived beforehand''. Quantum states that have the same energy have the same probability. To a given macrostate of the system there does in general correspond a large number of microstates, and it seems natural to assume that at any time *t* the system is equally likely to be in any one of these microstates. The quantity $w(N;V;E)$ will be defined as the actual number of possible microstate.

Comment 1: *The Boltzmann Factor*: Consider two vessels of equal volume with equal temperature and pressure, each containing one mole of two different perfect gases. Let us further suppose that the two gases are separated by a partition. When we remove the partition we also introduce an element of randomness into the system. Because of this we may postulate a relationship between the entropy of the system and the randomness of the system, that is, $S = f(w)$, where w is the number of a priori probable states (microstates) accessible to the system. Because of the extensive property (S and w are state variables) of the entropy, then

$$S_{tot} = S_1 + S_2 = f(w_1) + f(w_2). \qquad\qquad\qquad (a)$$

However, because the systems are independent, the number of a priori equally probable states is $w_{tot} = w_1 w_2$ so that

$$S_{tot} = f(w_1 w_2). \qquad\qquad\qquad (b)$$

Consequently, S must have the form: $S = k \ln w + c$, where k and c are constants. It can be seen that c must be zero.

Assembly (=System) It a number *N* of identical entities, such as molecules, atoms, electrons, etc.

Configuration (=macrostate of a system) Specified by the number of particles in each of the energy levels of the system.

Microstate of a system) Specified by the number of particles in each of the energy state.

- *Postulate 1: For a system in equilibrium all microstates are equally probable.*
- *Postulate 2: The observed macrostate is the one with the most microstates.*

Probability in Statistical Mechanics

Lemma I: The number of permutation of *N* distinguishable particles is *N*!

Lemma II: The number of ways of assigning *N* distinguishable particles into r distinguishable cells so that there are $N_1,......,N_r$ particles in the respective cells is

$$\frac{N!}{\prod_{i=1}^{r} N_i!}.$$

Lemma III: The number of ways of selecting *g* indistinguishable particles from a set of *N* distinguishable particles is $\binom{N}{g} = \dfrac{N!}{g!(N-g)!}$.

Lemma IV: given g indistinguishable cells and *N* indistinguishable particles, the number of ways of putting the *N* particles into the g cells when there is no restriction as to the number of particles in any one of the cells is $\dfrac{(N+g-1)!}{(g-1)!N!}$.

Lemma V: The number of ways of putting *N* distinguishable particles into *g* distinguishable cells is g^N.